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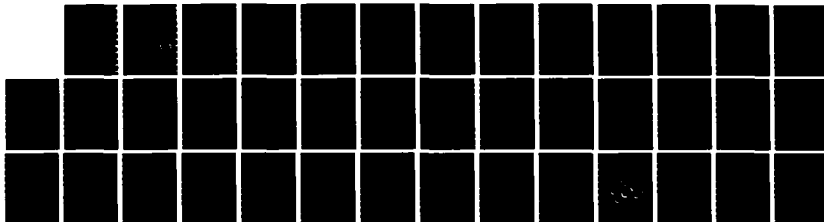
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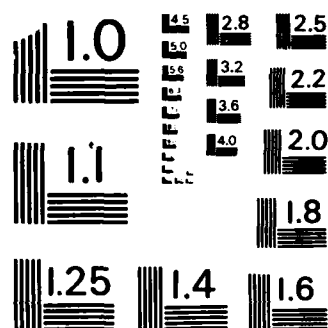
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TECHNICAL REPORT NO. 5

Reactions of Carbon Dioxide with the
Electron Rich Polyhydride Complex $[\text{Mo}(\text{dmpe})_2 \text{H}_4]$

by

Lawrence K. Fong, James R. Fox, and N. John Cooper*

Prepared for Publication

in

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Block 20, Abstract

Molybdenum

The electron rich polyhydride complex $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (1), formed by reduction of $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$ under H_2 , reacts with CO_2 to give a complex manifold of products containing formate, carbon dioxide and carbonate ligands. The final product of the reaction is $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$ (2), in which reductive disproportionation of CO_2 has led to a formation of a carbonate ligand. Two other products have been identified in which only two of the initial hydrides have been retained, one of which is the crystallographically characterized bis-formate $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ (3). The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.842(8) \text{ \AA}$, $b = 13.830(4) \text{ \AA}$, $c = 9.910(3) \text{ \AA}$, $\beta = 104.45(2)^\circ$, $\rho_{\text{calc}} = 1.38 \text{ g cm}^{-3}$, $Z = 4$, and $R_w = 3.96\%$ and has an octahedral geometry with trans η^1 -formate ligands. A precursor to 3 containing an η^2 - CO_2 ligand has been spectroscopically characterized as $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$ (4). Two complexes formed early in the reaction sequence, before elimination of H_2 , have been spectroscopically identified as $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3]$ (5) and $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ (6). The characteristic absorptions between 1600 and 2800 cm^{-1} of the formate, carbonate, hydride, and carbon dioxide ligands in these molecules have been assigned on the basis of ^{13}C and deuterium labelling studies.



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Introduction

Two of the characteristic reactions of carbon dioxide with transition metal complexes are reversible insertion into a transition metal hydride bond and reductive disproportion into carbonate and carbon monoxide by electron rich transition metal complexes.¹ While examining² the chemistry of molybdenum complexes with the strongly σ -donating bis-chelate phosphane $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ (dmpe) we have prepared an electron rich polyhydride complex $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (1) which could a priori exhibit either of these reactions when treated with CO_2 . In practice the polyhydride nature of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ allows the compound to undergo a complex series of reactions with CO_2 in which both reactivity patterns are observed. We have been able to identify most species within the reaction manifold, despite the lability of many of the complexes. The products include the formate hydride $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$, the carbonate hydride $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$, the CO_2 complex $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$, and the bis-formate complex $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ (isomeric with the CO_2 complex) -- a rare example of a structurally characterized η^1 -formate complex and the only reported bis-formate which does not form a polymeric structure.

Experimental Section

General. All manipulations were carried out under a dry, oxygen free atmosphere of argon except where stated otherwise. Solvents were freshly distilled from drying agents before use as follows: sodium benzophenone ketyl for tetrahydrofuran (THF); LiAlH_4 for pentane; CaH_2 for toluene and benzene. 40% sodium amalgam was prepared by the literature method.³ $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$ was prepared as reported previously.² $^{13}\text{CO}_2$ (92 atom per cent) was used as purchased from Merck, Sharpe, and Dohme. ^1H NMR spectra were recorded on a Bruker WM-300 at 300 MHz or a Bruker AM-500 at 500 MHz using the residual protons of the deuterated solvents as internal standards. ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WM-300 at 74.47 and 121.5 MHz respectively using the ^{13}C absorptions of the C_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$ solvents at δ 128.0 and 137.5 δ and the ^{31}P absorption of external 85% H_3PO_4 as calibrants. Microanalyses were performed

as indicated by Schwarzkopf Microanalytical Laboratory, Woodside, NY (Sch) or Galbraith Laboratories, Knoxville, TN (Gal). Gas chromatographic analyses for H₂ were carried out on a Perkin Elmer Sigma 300 using a 10.5' Carbosieve S-II column and TCD detection. Mass spectra were recorded on an AEI-MS9 using electron ionization at 60 eV. IR spectra of mull samples were recorded on a Perkin Elmer 457A or 683, and solution IR spectra were recorded on a Nicolet 7199 FT spectrometer. All IR spectra were calibrated relative to the absorption of a polystyrene film at 1601 cm⁻¹.

IR data are tabulated in the Results and Discussion section and have been omitted from the Experimental Section in the interests of brevity and clarity. Details of the preparation of ¹³C and D labelled samples have been omitted from the Experimental Section unless they differ significantly from the preparations of the analogous unlabelled material (this was sometimes the case when changes in reaction stoichiometry necessitated other changes in the reaction conditions).

[Mo(dmpe)₂H₄] (1). This compound was prepared and manipulated under an atmosphere of H₂, and exposure to ambient light was minimized. A solution of trans-[Mo(dmpe)₂Cl₂]² (0.97 g, 2.09 mmol) in THF (20 mL) was added to ca 12 g of 40% sodium amalgam under 20 mL of THF and placed under 1.5 atmospheres H₂. The mixture was vigorously stirred magnetically for 24 h and then allowed to settle for 12 h. The olive green solution was decanted off. Removal of the solvent gave a solid which was extracted with pentane (3 x 30 mL) to give a yellow-green solution. This was filtered and concentrated until saturated. Slow cooling (24 h) to -78°C gave pale yellow cubes which were collected by filtration and shown to be 0.64 g (1.59 mmol ≡ 77%) of [Mo(dmpe)₂H₄]: ¹H NMR (300 MHz, C₆D₆) δ 1.41 (br s, 32, dmpe), -5.51 (quin., J_{P-H} = 31.5 Hz, 4, Mo-H); ³¹P {¹H} NMR (C₆D₆) δ 51.0 (s). Anal. Calcd for C₁₂H₃₆MoP₄: C, 36.01; H, 9.07. Found (Sch): C, 36.27; H, 8.35.

[Mo(dmpe)₂(CO₃)H₂] (2). A pale yellow solution of [Mo(dmpe)₂H₄] (0.435 g, 1.08 mmol) in benzene (30 mL) was degassed and placed under 20 psi of CO₂ to give a burgundy brown solution. This was stirred in the dark for 13.5 h to give a golden brown solution from which a non-condensable gas shown to be H₂ (GC) was removed by use

of a Toepler pump (19.3 mL, 0.86 mmol). A further 10 mL of benzene was added to redissolve a small quantity of a brown precipitate, and pentane (100 mL) was carefully layered on to the benzene. Diffusive mixing over 11 days in the dark led to precipitation of $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$ (0.106 g, 0.23 mmol \equiv 21%) as a mixture of brown nuggets and yellow needles which were shown to be identical by comparison of ^1H and ^{31}P NMR spectra of mechanically separated samples. Analytical samples were prepared by recrystallization from benzene/pentane over 24 h: ^1H NMR (500 MHz, C_6D_6) δ 1.12-1.17 (c, 32, dmpe), -6.23 (dq, $J = 49, 43$ Hz, 2, Mo-H); ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6) δ 53.7 (t, $J = 8.5$ Hz, 2), 30.8 (t, $J = 8.5$ Hz, 2). Anal. calcd for $\text{C}_{13}\text{H}_{34}\text{MoO}_3\text{P}_4$: C, 34.07; H, 7.48; P, 27.04. Found (Gal): C, 33.75; H, 7.45; P, 28.28.

Reaction of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with $^{13}\text{CO}_2$ in Benzene and Preparation of $[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_3)\text{H}_2]$. A pale yellow solution of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (0.048 g, 0.12 mmol) in benzene (10 mL) in a 40 mL vessel was degassed and $^{13}\text{CO}_2$ (41.2 mL, 1.84 mmol) condensed into the vessel at -196°C . The vessel was slowly warmed to ambient temperatures and FT IR spectra of an aliquot were recorded after 7 and 21 min. The remainder of the solution was pressurized to 20 psi with Ar and stirred in the dark for 5.5 days. ^{31}P and ^{13}C spectra of the sample were recorded, and the solvent removed to give $[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_3)\text{H}_2]$ as a yellow brown solid (null IR). ^{13}C NMR (C_6D_6) δ 163.3 (t, $J_{\text{P-C}} = 9$ Hz, CO_3^{2-}); ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6) δ 53.7 (t, $J = 8.5$ Hz, 2), 30.8 (t of d, $J = 8.5$ Hz, $J_{\text{P-C}} = 8$ Hz, 2).

$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ (3). A pale yellow solution of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (0.046 g, 0.11 mmol) in pentane (20 mL) was placed under 20 psi of CO_2 and left in the dark with minimal agitation for 10 days. The solution was then filtered under CO_2 and cooled to 0°C under 20 psi CO_2 . Light brown crystals began to form after 12 h, and a first crop (0.015 g) was collected by filtration after 4.5 days. A second crop (0.011 g) was collected after 60 days, and the combined solids dried under vacuum to yield 0.026 g (0.05 mmol \equiv 47%) of $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$: ^1H NMR (300 MHz, C_6D_6) δ 8.36 ($w_{1/2} = 84$ Hz, 8, CH_2), -9.63 ($w_{1/2} = 124$ Hz, 24, CH_3); mass spectrum, m/e (parent ion) 488 (for ^{98}Mo); μ_{eff} (NMR method,⁴ toluene, 5% TMS, diamagnetic correction⁵) 2.54 BM.

Anal. calcd for $C_{14}H_{34}MoO_4P_4$: C, 34.58; H, 7.05; P, 25.48. Found (Sch) C, 34.51; H, 7.04; P, 25.68.

$[Mo(dmpe)_2(CO_2)(OCHO)H]$ (4). The pentane/benzene supernatant from the preparation of 2 above was concentrated to dryness under reduced pressure to give a brown solid, which was redissolved in 1:1 toluene:pentane (30 mL). The solution was cooled over 12 h to $-78^\circ C$ to initiate crystallization, and the light orange, irregular cubes which formed were collected after 3 days at $-78^\circ C$ and dried under vacuum to give 0.182 g (0.37 mmol \equiv 34 %) of a mixture containing (IR) traces of $[Mo(dmpe)_2(OCHO)_2]$ mixed with $[Mo(dmpe)_2(CO_2)(OCHO)H]$: 1H NMR (300 MHz, C_6D_6) δ 8.71 (s, 1, OCHO), 2.0 - 0.5 (c, 32, dmpe), -6.18 (quin, $J_{P-H} = 38$ Hz, 1, Mo-H); ^{31}P (1H) NMR (C_6D_6) δ 45.8 (s, dmpe); ^{13}C NMR (sample prepared from $^{13}CO_2$, C_6D_6) δ 224.6 (quin of d, $J_{P-C} = 12$ Hz, $J_{C-H} = 6$ Hz, CO_2), 167.2 (d, $J_{C-H} = 195$ Hz, OCHO). Anal. calcd for $C_{14}H_{34}MoO_4P_4$: C, 34.58; H, 7.05; P, 25.48. Found (Sch) C, 34.57; H, 6.99; P, 25.19.

The Initial CO_2 Adduct (5). A filtered solution of $[Mo(dmpe)_2H_4]$ (0.224 g, 0.56 mmol) in pentane (30 mL) was degassed, placed under 20 psi of CO_2 , and vigorously stirred magnetically in the dark. Within 1 h the solution changed from a pale yellow color to a burgundy brown and began to deposit a yellow solid. After 4 days the solution was light green and precipitation of the solid had ceased. The solid was collected by decantation, washed with pentane (20 mL) and dried under vacuum to give 0.073 g of yellow solid (0.16 mmol \equiv 29%). See Results and Discussion for description of ^{31}P and 1H NMR. ^{13}C NMR (sample prepared from $^{13}CO_2$, $C_6D_5CD_3/C_6H_5CH_3$, 195 K) δ 203.8 (d of t, $J = 26$ and 13 Hz, CO_2), 166.8 (d, $J_{C-H} = 195$ Hz, OCHO).

Preparation of D and ^{13}C Substituted CO_2 Adduct and $[Mo(dmpe)_2(OCHO)_2]$. In a typical procedure a solution of $[Mo(dmpe)_2H_4]$ (0.074 g, 0.56 mmol) in pentane (5 mL) was evacuated and $^{13}CO_2$ (37 mL, 1.66 mmol) was condensed into the vessel at $-196^\circ C$ from a high vacuum gas handling line. The sealed vessel was warmed to ambient temperatures and stirred for 3 days. The supernatant was removed by cannula filtration and the solid CO_2 adduct washed with pentane (10 mL) and dried under vacuum. The supernatant was concentrated under vacuum to give a yellow oil shown (IR)

to be primarily ^{13}C labelled $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ contaminated by some labelled $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$.

Formation of a Mixture of Solid $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ (6) and the Initial CO_2 Adduct. A degassed solution of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (0.037 g, 0.09 mmol) in benzene (5 mL) was swirled with CO_2 (20 psi) for 45 s and plunged into dry ice/acetone. The benzene was sublimed off over 20 h at -40 to -35°C and 10^{-3} torr to yield 0.029 g (0.06 mmol \equiv 66%) of a bright yellow mixture (mull IR) of the initial CO_2 adduct and $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$: ^1H NMR of sample prepared from $^{13}\text{CO}_2$ (300 MHz, C_6D_6 , 283 K) δ 8.87 (d, $J_{\text{C-H}} = 196$ Hz, 2, OCHO), 2.0 - 0.5 (c, 32, dmpe), -7.80 (c, 2, Mo-H); (300 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, 200 K) δ 8.89 (d, $J_{\text{C-H}} = 196$ Hz, 2, OCHO), 1.6 - 0.6 (c, 32, dmpe), -8.10 (quin, $J_{\text{P-H}} = 48$ Hz, 2, Mo-H); ^{31}P (^1H) NMR (C_6D_6) δ 54.2 (t, 2, $J = 14.5$ Hz), 29.1 (t, 2, $J = 14.5$ Hz); ^{13}C NMR (sample prepared from $^{13}\text{CO}_2$, C_6D_6) δ 167.1 (d, $J_{\text{C-H}} = 195$ Hz, OCHO).

X-Ray Crystallography: General. Crystals were handled under argon and sealed in glass capillaries for diffraction studies. The data were collected on a Nicolet R3 diffractometer using graphite-monochromated Mo K α radiation. The final unit cell parameters were determined by a least squares treatment of the setting angles of 12 sets of accurately centered Friedel pairs. Lorentz and polarization corrections were applied using the SHELXTL programs.⁶ Atomic scattering factors were based on literature values for Mo⁷ and on those in the SHELXTL program for other atoms. Weights were taken as: $w = (\sigma^2(F) + g F^2)^{-1}$.

Structure Solution and Refinement. Crystals of $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ suitable for a single crystal X-ray diffraction study were prepared by recrystallization from pentane. The parallelepiped-shaped crystal studied measured approximately 0.25 mm on each side. Reflections taken from a rotation photograph indicated that the unit cell had two angles measuring approximately 90° ; the monoclinic symmetry was confirmed by the presence of mirror symmetry uniquely along the b-axis in axial photographs. No higher order unit cell could be found with either the P3 program or with TRACER. A trial data collection indicated the unit cell to be $P 2_1/n$, and a single quadrant of

data {(hkl): +h, +k, ±l} was collected. Full details of the data collection are presented in Table I. No decrease in intensity was observed for the check reflections during data collection. The position of the Mo (which was known to be on a special position) and of the atoms bound directly to Mo were revealed by the SOLV direct methods of SHELXTL.⁶ Refinement of atomic positions revealed the positions of all non-hydrogen atoms on subsequent difference maps. The hydrogens of the dmpe ligands were placed in positions (Table S-II in the Supplementary Material) calculated from those of the adjacent carbon atoms with $r(\text{C-H}) = 0.96 \text{ \AA}$ and $U_{\text{iso}} = 1.2 \times U_{\text{equiv.}}$; the methyl hydrogens were refined as free-to-rotate rigid groups. The formate hydrogen, Ha, was located in a difference map after all other hydrogen atoms had been placed in their calculated positions. The positional parameters of the formate hydrogen were allowed to refine, and led to a reasonable C-H bond distance (0.99(6) Å) from the formate carbon, Ca, with the expected large e.s.d.'s in its positional parameters. Refinement was continued to convergence ($\Delta/\sigma < 0.1$) using the blocked-cascade least-squares procedure of SHELXTL. Final atomic positional parameters are presented in Table II and anisotropic thermal parameters are given in Table S-I of the supplementary material.

Results and Discussion

The reaction of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with CO_2 is complex, and leads to a manifold of six observable products. Identifying these species is complicated by the tendency of many to convert to species later in the sequence under typical separation conditions. We have, however, been able to use the sensitivity of the reaction to the nature of the solvent and other reaction variables to isolate analytical samples of three of the compounds, and with the spectroscopic characteristics of these materials to hand we have been able to identify two of the remaining complexes in the system. After a brief discussion of the synthesis of the starting tetrahydride 1 the characterization of the isolable products of the reaction of 1 with CO_2 will be presented, and the probable nature of some of the more labile intermediates in the reaction will then be

discussed.

Preparation of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (1). A number of eight-coordinate tetrahydrido-tetraphosphane complexes of molybdenum have been prepared by hydride reduction of Mo(IV) $[\text{MoCl}_4\text{L}_2]$ complexes in the presence of excess phosphane^{8,9} or by addition of H_2 to Mo(0) $[\text{Mo}(\text{PAR}_2\text{CH}_2\text{CH}_2\text{PAR}_2)_2(\text{N}_2)_2]$ complexes.¹⁰ The ability of 40% sodium amalgam to reduce $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$ ² suggested that a similar complex might be available with dmpe as a chelating diphosphane ligand by conducting the reduction under H_2 . This proved to be the case, and thermally stable but highly air sensitive 1 could be prepared in 77% yield in this manner. The complex does not give a parent ion in the mass spectrum (the highest peak corresponds to $[\text{Mo}(\text{dmpe})_2\text{H}_2]^+$), but was unambiguously characterized as a tetrahydride by ^{31}P NMR spectra: the singlet observed at δ 51.0 in broad band ^1H decoupled spectra splits into a quintet¹¹ when the decoupling irradiation was reduced to a narrow band of frequencies centered at δ 1.5.

Isolation and characterization of $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$ (2). The final product of the reaction of 1 with CO_2 under most conditions is the unusual carbonate dihydride 2, which can be isolated in analytically pure form when the reaction is carried out in benzene.

Formulation of the product as $[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2]$ is consistent with the ^1H and ^{31}P NMR spectra of the complex. The high field absorption assigned to the hydride ligands in ^1H NMR spectra could be interpreted on the assumption that four ^{31}P and two ^1H nuclei formed an $\text{AA}'\text{M}_2\text{XX}'$ spin system ($\text{X}, \text{X}' = \text{H}$) with $J_{\text{AM}} = J_{\text{A}'\text{M}} = 8.5$ Hz, $J_{\text{AX}} = J_{\text{A}'\text{X}} = J_{\text{MX}} = J_{\text{MX}'} = 43$ Hz, $J_{\text{AX}'} = J_{\text{A}'\text{X}} = 49$ Hz, $J_{\text{AA}'} < 2$ Hz, $J_{\text{XX}'} < 2$ Hz.¹² The ^{31}P (^1H) NMR spectrum of the compound contained two triplet resonances as anticipated on this model, and the presence of two hydride ligands was confirmed by reducing the ^1H decoupling irradiation to a narrow band of frequencies centered at δ 1.5. This gave a ^{31}P spectrum in which the two dmpe resonances appeared as partially resolved triplets of triplets¹⁴.

The CO_2 derived ligand was identified as a carbonate group by NMR and IR studies of 2 and of ^{13}C and D labelled samples. ^{13}C NMR spectra of a sample prepared from 92%

enriched $^{13}\text{CO}_2$ contained a triplet at δ 163.3 assigned to the carbonate carbon selectively coupling to two of the dmpe P nuclei with $J_{P-C} = 9$ Hz. This interpretation was supported by the ^{31}P NMR spectrum of this sample, in which the δ 53.7 peak showed the corresponding doublet pattern but the δ 30.8 peak was unchanged. An alternative assignment of the carbon resonance to a formate ligand (which could absorb in the same region — see below) was ruled out by two observations: the ^{13}C resonance of 2 did not exhibit the single bond ^1H coupling characteristic of formates (see below) in gated spectra, and the principal $\nu_{C=O}$ for the carbonate ligand at 1601 cm^{-1} shifted 40 cm^{-1} with ^{13}C substitution but was unaffected by deuterium substitution.¹⁵

Isolation and Characterization of $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ (3). The bis-formate complex was isolated as an analytically pure crystalline material by reacting $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with CO_2 in pentane under conditions such that agitation of the solution was minimized. The complex was primarily characterized by a single crystal X-ray diffraction study, which established that the complex has two η^1 -formate ligands arranged in a trans geometry as illustrated in Figure 1. The bond lengths and bond angles within the complex are presented in Table III and IV respectively, and details of the structure determination are given in the Experimental Section and in the Supplementary Material.

The η^1 -formate ligands are the most interesting feature of the structure. Formate, like most carboxylate ligands, tends to be a bis-chelate or bridging ligand, and relatively few η^1 -formate complexes have been structurally characterized to date.¹⁶ The Mo-Ox(2) distance of $3.540(8)\text{ \AA}$ is unambiguously non-bonding, and, as in the case of most (but not all^{16d,e}) of the reported η^1 -formate structures, the C-O bond lengths are consistent with the conventional bonding description ($\text{MoO}-\text{CH}=\text{O}$). The failure of the formate ligands to bridge Mo^{2+} sites in the lattice contrasts markedly with the polymeric structures established for the formate dihydrates¹⁷ and anhydrous formates¹⁸ of many divalent metals, and with the extensive chemistry of dinuclear Mo(II) carboxylates with quadruple metal-metal bonds.¹⁹

Initial characterization of 3 was hampered by its paramagnetism, which corresponds to an effective magnetic moment in solution of 2.54 BM. This is close to the spin only value for an approximately octahedral d^4 complex with two unpaired electrons and no major Jahn-Teller distortion, and is consistent with the observed solid state structure. It is also similar to the value which we have reported for the closely related molecule trans-[Mo(dmpe)₂Cl₂], and, as in that case, the dmpe ligands of the molecule give rise to observable (although broad) resonances in ¹H NMR spectra despite the paramagnetism of the molecule. Similar behavior has been reported for other d^4 -octahedral complexes²⁰ and demonstrated to result from the temperature independent paramagnetism of the complexes.²¹ A similar interpretation may apply in the present case, although detailed magnetic and NMR studies would be required to confirm this.

Characterization of [Mo(dmpe)₂(CO₂)(OCHO)H] (4), a Precursor to [Mo(dmpe)₂(OCHO)₂]. The most logical immediate precursor to the bis-formate 3 would be a complex containing one formate ligand, one CO₂, and a hydride ligand, and we have indeed been able to obtain evidence for the intermediacy of a complex formulated as [Mo(dmpe)₂(CO₂)(OCHO)H] (4) in the formation of 3. The complex was obtained from the mother liquor of the pentane/benzene mixture from which 2 precipitated, and could be isolated by stripping this solution, redissolving the material in a toluene/pentane mixture, and cooling the new solution slowly to -78°C. Complex 4 converts into 3 rapidly in solution and slowly in the solid state, and we have been unable to obtain solutions of the material which do not contain significant quantities of 3. Mull IR spectra do, however, indicate that fresh solid samples are relatively clean, and elemental analysis of this material is consistent with that expected for a mixture of the isomeric species 3 and 4.

The presence of a single hydride ligand and two dmpe ligands in 4 was established by the combined ¹H and ³¹P spectra of an NMR sample of the solid prepared under CO₂ in C₆D₆. The ³¹P {¹H} spectrum contained a single resonance attributable to 4, which was split into a doublet in spectra recorded with narrow band decoupling (centered at δ 1.5) of the dmpe protons. The presence of a high field quintet of the appropriate

intensity in ^1H NMR spectra confirmed that this doublet splitting was a consequence of coupling to a single metal hydride, and that all four dmpe P nuclei are equivalent. Since it is unlikely that the ground state structure of the complex contains chemically equivalent P nuclei, this indicates that the molecule is fluxional.²² The magnitude of $J_{\text{P-C}}$ in 4 was similar to that observed in 1.

The presence of a coordinated CO_2 ligand in 4 was suggested by examination of ^{13}C NMR spectra of a solution prepared by reacting 1 with 5 equivalents of 92% enriched $^{13}\text{CO}_2$ for 10 days in d_6 -benzene in a sealed NMR tube. In addition to the carbonate resonance of 2 (the principal product under these conditions) and resonances assigned to 6 (see below) the ^1H decoupled spectrum contained a singlet at δ 167.2 and a quintet ($J = 12$ Hz) at δ 224.6. In ^1H coupled spectra the singlet exhibited single bond coupling of 195 Hz, consistent with assignment to a formate ligand, while the quintet showed only weak long range coupling ($J_{\text{C-H}} \approx 6$ Hz) to the hydride on Mo. This indicates that the second ligand is not a formate, and assignment as an $\eta^2\text{-CO}_2$ ligand containing a C directly bonded to Mo is consistent with the observed P-C coupling²³ and leads to a reasonable 18-electron configuration for the complex. Assignment of the δ 224.6 resonance to a carbonate ligand, which would also lack a directly bonded hydrogen, is implausible on two counts: (a) long range coupling to a metal hydride is unlikely in a carbonate complex (and is not observed in 2); (b) this chemical shift is more plausibly associated with a CO_2 ligand than a carbonate (see below).

An alternative formulation in which the CO_2 acts as an η^1 (Lewis acidic) ligand and the formate as a bis-chelate ligand is difficult to reconcile with the IR characteristics of the complex (see below), since the CO_2 stretching frequencies are in the correct region for an $\eta^2\text{-CO}_2$ and would be high for an $\eta^1\text{-CO}_2$ (c. f. 1740 cm^{-1} for $[\text{Ni}(\text{PCy}_3)_2(\text{CO}_2)]$ ²⁴ and 1610 cm^{-1} for $[\text{Rh}(\text{diars})_2(\text{CO}_2)\text{Cl}]$ ²⁵). $\nu_{\text{C=O}}$ for the formate is also in the correct region for an η^1 -formate (see below) and would be high for a bis-chelate formate.

The Initial CO_2 Adduct, $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3]$ (5). The complexes discussed so far occur late in the sequence of reactions which follow addition of CO_2 to

[Mo(dmpc)₂H₄] (1), and are all formed after the loss of one molecule of H₂ from the starting tetrahydride. We have also, however, obtained evidence for the formation of two complexes which, in stoichiometric terms, involve the addition of two molecules of CO₂ to 1. The first of these probably contains a coordinated CO₂ and is one of the most interesting molecules in the system. Unfortunately, however, it is also one of the most labile and has only been partially characterized.

The initial CO₂ adduct can be reproducibly obtained as a solid by reaction of 1 with CO₂ in pentane. As reported above this reaction gives a solution of 3 over a period of 10 days if care is taken to avoid agitating the reaction. If, however, the solution is magnetically stirred, a yellow precipitate is formed which can be collected after 3 to 5 days in 29% yield.²⁶ A Nujol mull of this material has a distinctive IR spectrum, one feature of which is a weak band at 1843 cm⁻¹ indicative of the presence of Mo-H groups (c. f. 1800 cm⁻¹ in 2).

NMR spectra in benzene were of limited utility in characterizing this material. The principal absorption in the high field region of the ¹H NMR spectrum of a freshly prepared solution in d⁶-benzene did exhibit a quintet at δ -5.07, confirming the presence of one or more hydride ligands coupled to four equivalent ³¹P nuclei. The complex was, however, unstable in this solvent, decomposing in ca. 30 minutes to another complex (see below) which was itself labile. ³¹P NMR spectra of this sample did not exhibit any resolved resonances attributable to the initial adduct, but there was a broad hump from δ 32 to 45 of considerable integrated intensity which decayed on a similar time scale to the high field hydride. This suggested that the symmetry of the hydride resonance, as in the case of the CO₂ complex 4, reflected a low energy fluxional process which happens to be too slow to equilibrate the P resonances at 298 K. This interpretation was confirmed by ³¹P NMR spectra in d⁸-toluene at 200 K of a sample of the adduct prepared in situ by reaction of 1 with ¹³CO₂. This exhibited a well resolved but complex spectrum, which appears to be that of the complex below the low temperature limit, but which could not be analyzed in detail since it was partially obscured by absorptions of unreacted 1 and of small quantities of materials

later in the reaction sequence.

The most informative spectra of the initial adduct were ^{13}C NMR spectra in d^8 -toluene/toluene at 195 K of the ^{13}C enriched sample prepared in situ. In addition to a formate resonance at δ 174.9 ($J_{\text{C-H}} = 192$ Hz — this resonance will be discussed below), these contain a complex resonance at δ 203.8²⁷ which lacks single bond coupling to H in undecoupled spectra and a resonance of equal intensity at δ 166.8 with $J_{\text{C-H}} = 195$ Hz in undecoupled spectra. These resonances indicate the presence of a coordinated CO_2 and of a formate ligand,²⁸ and suggest that the complex is most probably $[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3]$ (5).²⁹ Similar resonances³⁰ could be observed in ^{13}C spectra recorded in d^6 -benzene, and these decayed at a rate similar to that of the ^1H and ^{31}P resonances of 5 under these conditions.

The initial adduct should be considerably more stable in pentane than in benzene or toluene, since its preparation took several days in this solvent. This was confirmed by examining ^{31}P and ^{13}C NMR spectra of a solution of 1 in pentane sealed in an NMR tube under 92% enriched $^{13}\text{CO}_2$. Resonances very similar to those of 5 in aromatic solvents were observed, and had a lifetime of days at ambient temperatures.³¹

The null IR spectrum of 6 (see below) provides the only ambiguity in its spectroscopic characteristics. In addition to the Mo-H stretching absorption mentioned above the spectrum contains absorptions at 1628 and 1612 cm^{-1} which probably arise from stretching modes of C=O bonds. Assignment of the 1612 cm^{-1} band to the formate C=O bond was confirmed by characteristic isotope shifts of 38 and 10 cm^{-1} respectively following ^{13}C and D substitution, but assignment of the 1628 cm^{-1} band to the coordinated CO_2 , although supported by the ^{13}C isotope shift of 40 cm^{-1} , was apparently inconsistent with an isotope shift of 4 cm^{-1} following D substitution. It should be noted, however, that this is much smaller than the 10 cm^{-1} secondary isotope effect observed for other formate absorptions in this system, and the shift probably occurs because 1628 cm^{-1} band has been shifted from its true position by Fermi resonance with the 1612 cm^{-1} band. This interpretation is strongly supported by the lack of any D shift for the corresponding absorption in pentane, which at 1685 cm^{-1} is

much further from the formate band.

Formation of $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ (6). As mentioned above, the initial CO_2 adduct converts rapidly into a new complex, which is itself labile with respect to conversion to 4, 3, and eventually 2, in benzene or toluene at ambient temperatures. Although it was too labile to allow isolation of analytical samples, a mixture of the new complex and 5 could be obtained in the solid state by swirling a benzene solution of 1 under CO_2 (20 psi) for 45 sec, freezing the solution and subliming off the benzene at -40°C .

NMR spectra recorded in d^6 -benzene³² established that the new complex was $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ (6). The presence of two triplets in ^{31}P $\{^1\text{H}\}$ spectra indicated that there are two chemically distinct types of dmpe P, and the further triplet splitting in spectra recorded with narrow band decoupling of the dmpe protons (centered at δ 1.5) suggested the presence of two hydride ligands on the Mo. This was confirmed by analysis of the complex absorption in ^1H NMR spectra at δ -7.8 assigned to the metal hydrides, which indicated that the four ^{31}P and two ^1H nuclei form an $\text{AA}'\text{M}_2\text{XX}'$ spin system ($\text{X}, \text{X}' = \text{H}$) with $J_{\text{AM}} = J_{\text{A}'\text{M}} = 14.5$ Hz, $J_{\text{AX}} = J_{\text{A}'\text{X}'} = 45$ Hz, $J_{\text{MX}} = J_{\text{MX}'} = 59$ Hz, $J_{\text{AX}'} = J_{\text{A}'\text{X}} = 52$ Hz.³³ ^1H NMR spectra also contained a resonance at δ 8.87 (equal in intensity to the hydride resonances and with a ^{13}C coupling of 196 Hz appropriate for single bond coupling to an sp^2 C) which suggested the presence of two formate ligands. This was confirmed by the ^{13}C $\{^1\text{H}\}$ spectrum of a ^{13}C enriched sample which consisted of a single resonance at δ 167.1 which split into a doublet with $J_{\text{C-H}} = 195$ Hz in the absence of ^1H decoupling.

Attempts to Crystallographically Characterize the Initial CO_2 Adduct. The ability to prepare solid samples of the initial CO_2 adduct, together with limited number of structurally characterized CO_2 complexes, led to extensive efforts to characterize the adduct crystallographically. Diffraction quality crystals were prepared from a sample of 1 in pentane which was stirred under CO_2 for 24 h. After removal of the precipitated 5 by filtration, the unstirred mother liquor deposited orange brown cubic crystals over a period 48 h. The IR spectrum of a Nujol mull of these crystals established that the bulk of the sample was 5 rather than 6, and a diffraction study

was attempted. This suggested that the complex contained two dmpe ligands, two hydrides, a formate, and an η^1 -O coordinated CO₂. The latter is an unprecedented coordination mode for CO₂, but this cannot be the correct structure since "[Mo(dmpe)₂(CO₂)(OCHO)H₂]" would be a paramagnetic complex while 5 and 6 are diamagnetic and the bulk of the crystalline sample was established to be diamagnetic by a Faraday balance measurement. It seems probable that the "CO₂" ligand is in fact a formate, and that an initial crystal of 5 converted to 6 before or during the diffraction study,^{34, 35} but despite extensive efforts experimental difficulties prevented us from obtaining evidence supporting this hypothesis, and little weight can be attached to the diffraction results.³⁶

¹³C NMR Characteristics of Carbon Dioxide, Formate and Carbonate Ligands. We have based distinctions between coordinated CO₂ ligands, formates and carbonates on less ambiguous data than chemical shifts (such as the large single bond J_{C-H} anticipated for formates), but it is reassuring to note that the resonances assigned to CO₂ ligands in 4 and 5 occur in the δ 200 to 230 region in which such resonances have been previously observed (δ 206.1, Mo(CO₂)₂(PMe₃)₄)³⁷ and δ 220.5, [Nb(η -C₅H₄Me)₂(CH₂SiMe₃)(CO₂)]³⁸). This is considerably downfield of free CO₂ (δ 132.2³⁹), and somewhat below where formate ([Re(η -C₅H₅)(NO)(PPh₃)(OCHO)]: δ 171.4⁴⁰) and carbonate ([UO₂]₃(CO₃)₆)⁴¹: δ 168.7 and 167.3⁴¹) resonances have been reported. It is clear that formates and carbonates can not be distinguished on chemical shift grounds,⁴² but the positions of the resonances assigned to coordinated carbonate in 2 and to formates in 4, 5, and 6 are consistent with the quoted literature values and with each other.

Infra Red Characteristics of the Functional Groups Produced in the Reaction between [Mo(dmpe)₂H₄] and CO₂. Metal hydride, formate, carbonate and coordinated CO₂ functional groups would all be expected to have characteristic IR absorptions in the region between 1600 and 2800 cm⁻¹. These absorptions were, however, of limited use in initial characterization of complexes formed from the reaction of [Mo(dmpe)₂H₄] with CO₂ partly because the functional groups have similar frequencies in many of the

complexes and partly because many of the absorptions were sensitive to the sample medium. It has subsequently proved possible, however, to use ^{13}C and D labelling studies to assign the IR absorptions of the complexes in the 1600 to 2800 cm^{-1} region, and the results of this analysis are presented in Table V. The assignments are consistent with the NMR and crystallographic studies, and, in some cases, as pointed out above, provide critical confirmation of the presence of certain functional groups.

Examining the effects of deuterium substitution on the IR spectra of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ derivatives was complicated because $[\text{Mo}(\text{dmpe})_2\text{D}_4]$ could only be obtained in, at best, ca 60 atom % purity. Reduction of $[\text{Mo}(\text{dmpe})_2\text{Cl}_2]$ with 40% sodium amalgam under D_2 invariably gave material containing Mo-H groupings (IR), and the presence of a broad band at 1975 cm^{-1} in the region characteristic of saturated C-D bonds suggested that this occurred because 1 is an exceptionally reactive C-H activation and exchange catalyst which catalytically deuterates its own dmpe ligands. It is not surprising that $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ is a C-H activation and exchange catalyst, given that the closely related early transition metal polyhydride $[\text{Ta}(\text{dmpe})_2\text{H}_5]$ undergoes facile hydride exchange with benzene.⁴³ The ability of the complex to activate the saturated C-H bonds of dmpe is, however, unusual, although $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{dmpe})\text{H}_3]$, a formally isoelectronic Mo (IV) complex, has been reported to catalyze exchange between hydrogen in ligated dmpe and deuterium in benzene- d_6 .⁴⁴ Further details of the characteristics of 1 as a C-H activation catalyst will be reported later.

Our initial assumptions when using labelled material to assign the IR absorptions of complexes were: that ^{13}C labelling of CO_2 , carbonate or formate ligands should shift their C=O stretching absorptions, and the C-H stretching absorptions of formate ligands, by an amount approximating that predicted by the simple harmonic oscillator model,⁴⁵ but should not affect the stretching absorptions of metal hydride bonds in the same molecule; that deuterium labelling of the metal hydrides should similarly affect metal hydride stretching absorptions and the C-H stretching frequencies of derived formates, but should not affect C=O stretching absorptions.

In practice, ^{13}C substitution shifted $\nu_{\text{C=O}}$ ca. 40 cm^{-1} for coordinated CO_2

(predicted 38 cm^{-1} for an absorption at 1700 cm^{-1}), 40 cm^{-1} for the carbonate (predicted 36 cm^{-1}), and ca. 38 cm^{-1} for the formates (predicted 36 cm^{-1} for 1612 cm^{-1} band). ^{13}C labelling also had the predicted small effect (8 cm^{-1}) on $\nu_{\text{C-H}}$ for formate ligands.

Deuterium labelling shifted $\nu_{\text{Mo-H}}$ as predicted, although it was not possible to determine by how much since the Mo-D region (ca. 1300 cm^{-1}) was obscured by stronger absorptions. Deuterium labelling also shifted $\nu_{\text{C-H}}$ for formates, but again the magnitude of the effect could not be determined, in this case because the weak formate C-D stretches could not be distinguished from the C-D stretches of partially deuterated dmpe (see above). Deuterium labelling did not change $\nu_{\text{C=O}}$ for carbonate or CO_2 ligands (with the exception of the solid state spectrum of the initial CO_2 adduct: see above). Formates did not completely conform to this elementary model, and exhibited small ($7 - 10\text{ cm}^{-1}$) shifts in the frequencies of the C=O stretching absorptions on deuterium substitution. These second order effects are not unreasonable in the case of η^1 -formate ligands, and are similar to those reported previously for a tungsten formate⁴⁶. The sensitivity of the formate $\nu_{\text{C=O}}$ to deuterium substitution assisted in many of the spectral assignments.

The overall positions of the metal hydride, formate, carbonate and coordinated CO_2 absorptions, as established by labelling studies, fall within the expected ranges. The metal hydride and coordinated CO_2 stretching frequencies are quite sensitive to the precise nature of each complex, and have overlapping ranges of 1679 to 1891 cm^{-1} and 1628 to 1787 cm^{-1} respectively. The principal carbonate absorption of 2 (1601 cm^{-1}) and the $\nu_{\text{C=O}}$ bands of the formates, with a narrow spread of 1614 to 1628 cm^{-1} , fall somewhat below these ranges but are themselves similar in energy. The positions of the formate absorptions are very similar to that of the η^1 -formate $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)(\text{OCHO})]^{40}$ (1616 cm^{-1}) and somewhat above those reported for bis-chelate transition metal formates (such as $[\text{Ru}(\text{PPh}_3)_3(\text{OCHO})\text{H}]$: $\nu_{\text{C=O}} = 1565\text{ cm}^{-1}$ ⁴⁷), as would be expected from the established effects of coordination mode on the IR spectra of carboxylate complexes.⁴⁸

Sequence of Formation of the Complexes Derived from the Reaction of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with CO_2 (Scheme I) and Evidence for the Formation of a Bis-Chelate Formate Complex $[\text{Mo}(\text{dmpe})_2(\text{OCHO})\text{H}]$ (7). The early stages of the reaction of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with CO_2 are sufficiently slow in pentane to permit the reaction to be monitored using the characteristic IR absorptions of the products from 1500 to 2400 cm^{-1} . Spectra of a solution of 1 recorded 1, 4.5, 8, and 20.5 h after exposure to an atmosphere of CO_2 established that only traces of unreacted 1 were left after 4.5 h (at which point the concentration of the initial CO_2 adduct 5 was at its maximum) and that all of the material had been converted to 6 or 3 (whose spectra can not be distinguished in this region in pentane) after 20.5 h.

IR spectra in pentane also, however, indicated the formation, at a rate comparable with the formation of 5, of a further complex characterized by a strong absorption at 1558 cm^{-1} . This is below the $\text{C}=\text{O}$ stretching region for η^1 -formates in this system, but within the range in which a bis-chelate formate might be expected to absorb. Assignment to a bis-chelate formate was supported by introduction of deuterium and ^{13}C labels, which shifted the absorption to 1548 and 1520 cm^{-1} respectively. The ^{13}C NMR resonance observed at δ 174.9 immediately after $^{13}\text{CO}_2$ was reacted with 1 in toluene/ d^8 -toluene at 195 K (see discussion above of the initial CO_2 adduct) is most reasonably assigned to the new formate complex, confirming that the complex is an early product in the reaction manifold in toluene as well as in pentane.

The bis-chelate formate was never obtained as a solid, and no conditions were discovered under which it was a major product of the reaction of 1 with CO_2 . The new complex may be $[\text{Mo}(\text{dmpe})_2(\text{OCHO})\text{H}]$ (7), but it is unclear where such a complex would fit into the reaction pathway (unless it provides an alternate pathway from 5 to 3 - see Scheme I), and in the absence of ^1H NMR or other data on the number of hydride ligands in the complex identification as 7 must remain tentative.

The synthetic results indicate that the other complexes which contain only two of the original hydride ligands (4, 3, and 2) are formed later in the reaction sequence than the complexes containing all four of the original hydrides (5 and 6). The

remaining hydrogen is lost as H_2 , and the rapidity with which 5 and 6 convert into complexes later in the reaction sequence in benzene is indicated by the observation that close to an equivalent of H_2 is evolved after only 13.5 h (see preparation of 2 in the Experimental Section). The loss of H_2 appears to be essentially irreversible, and we have seen no evidence for complexes 4, 3, or 2 reverting to complex 5 or 6.

Interconversions within the characterized complexes retaining only two of the original hydrides may be more complex. The conversion of 4 to 3 was observed in the solid state (IR), in benzene solution (1H NMR), and in pentane solution (IR) as indicated above. The surprisingly high yield of 4 (which was not a major species in in situ NMR studies) from pentane/toluene at $-78^\circ C$, however, suggests that this may be a reversible reaction, i. e. that although 4 was never the major species in the mixture it was isolated in good yield because it was the only species in the reaction manifold which was both insoluble and accessible under these conditions.

The carbonate complex 2 could reasonably be formed from the bis-formate 3 (although the reaction may require reversal of one of the $CO_2/Mo-H$ insertion reactions to give an intermediate CO_2 complex) and it was confirmed in a separate experiment that 3 converts into a mixture of 3 and 2 in benzene (IR) under 20 psi CO_2 over 7 days.

Conclusion

Although we have not determined the fate of the equivalent of CO which should be produced, the carbonate ligand in $[Mo(dmpe)_2(CO_3)H_2]$, the final product of the reaction of $[Mo(dmpe)_2H_4]$ (1) with CO_2 , is probably formed by reductive disproportionation of CO_2 by an electron rich intermediate species which acts as if it contains " $[Mo(dmpe)_2H_2]$ ". The availability of such a species indicates that the insertions of CO_2 into Mo-H bonds which result in the formation of the formate ligands in precursors such as 3, 4, 5, and 6 are readily reversible, as has been reported in the case of some other $CO_2/M-H$ insertions.^{47,49} It is the reversibility of the CO_2 insertions, together with the presence of four hydride ligands in 1, which allows the observation of such a wide range of intermediate formate and carbon dioxide complexes

from the reaction of 1 with CO₂.

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- (11) The splittings observed in ³¹P spectra during such experiments are typically less than the corresponding splittings in the ¹H spectra, as a consequence of partial decoupling of the hydrides on the metal.
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example, be mutually trans: strong coupling of these two spins would not significantly affect the anticipated spectrum), while the other (A) pair are magnetically inequivalent with respect to the metal hydrides. The magnetic inequivalence of the A ^{31}P nuclei and of the hydride ligands could, for example, be accounted for if A and A' are cis and X and X' are cis within a plane perpendicular to the M-Mo-M axis. Accidental degeneracy of J_{AX} and J_{MX} is not unreasonable within this model, since X would be cis with respect to the A ^{31}P and both M ^{31}P .

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- (22) Fluxionality would be anticipated for this molecule since it is probably seven coordinate. Reversible broadening of the ^{31}P resonance was observed when a sample of 4 was cooled to 200 K, but the low temperature limit could not be attained.
- (23) The ^{31}P (^1H) NMR spectrum of this sample, which incidentally confirmed the composition of the mixture of materials obtained under these conditions, exhibited the complementary splitting of the δ 45.8 resonance into a doublet with $J_{\text{P-C}} = 12$ Hz.
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- (26) The influence of agitation on the course of the reaction is probably a crystallization effect, in which stirring promotes nucleation of the initial adduct. The adduct is relatively stable if it is precipitated, but in solution rapidly converts to other species in the reaction sequence.
- (27) This resonance approximates a doublet of triplets, suggesting that four ^{31}P nuclei and the ^{13}C form an A_2BCX coupling system with $J_{\text{A-X}} = 13$ Hz, $J_{\text{B-X}} = 26$ Hz and $J_{\text{C-X}}$ too small to observe. This would be consistent with the complex nature of the ^{31}P spectrum, and the average $J_{\text{P-C}}$ of 13 Hz is similar to the value of 12 Hz observed for the CO_2 carbon in 4.
- (28) The formate resonance is coincident with that of 6 (see below), but ^{31}P spectra establish that this sample contains little 6. Conversely, we have ^{31}P and ^{13}C spectra of samples of 6 containing little 5.
- (29) We have no direct evidence for the number of hydride ligands in 5, but, if the CO_2 is an η^1 (Lewis acid) ligand, three hydrides would make 5 an 18 electron complex and distinguish 5 from 4.
- (30) δ 203.4 with $J_{\text{C-H}} = 0$, δ 167.1 with $J_{\text{C-H}} = 195$ Hz. The CO_2 resonance was a quintet with $J_{\text{P-C}} = 15$ Hz at 298 K.

- (31) δ 199.2 with $J_{C-H} = 0$, δ 165.5 with $J_{C-H} = 198$ Hz. As in the case of room temperature benzene spectra, the CO_2 resonance was a quintet with $J_{P-C} = 15$ Hz.
- (32) The best resolved NMR spectra of this molecule were obtained from material prepared from 92 % enriched $^{13}CO_2$, and were recorded in d^6 -benzene at 283 K. The complex was more stable in d^8 -toluene at 200 K, and integrations are based on spectra recorded under these conditions. These spectra were consistent with the benzene spectra except that the metal hydride absorption was less well resolved and approximated a quintet.
- (33) These coupling constants are physically reasonable, and led to a good PANIC* simulation of both the 1H and ^{31}P NMR spectra of the complex. The coupling scheme implies that one (M) pair of P atoms are chemically and magnetically equivalent while the other (A) pair are magnetically inequivalent with respect to the metal hydrides.
- (34) The structure would not refine when an additional hydrogen was added to the " CO_2 " ligand in the appropriate position to convert this into a formate ligand, but the structure also lacked a vacant site on the metal which could accommodate a third hydride.
- (35) The stability of 5 in the solid state was variable and depended on the sample. IR spectra of mulls indicated that some powdered samples converted to 6 in a matter of weeks, but crystalline samples were in general stable for months. Conversion to 6, may, however, be accelerated in the X-ray beam.
- (36) If the structure is that of $[Mo(dmpc)_2(OCHO)_2H_2]$, the coordination sphere is a distorted dodecahedron which approximates a tetrahedron of P ligands interpenetrated by a tetrahedral array of two hydrides and two formates. This would be consistent with the P and H ligands of 6 forming the observed $AA'M_2XX'$ coupling system.
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Table I. Summary of Crystallographic Data for $[\text{Mo}(\text{dmpc})_2(\text{OCHO})_2]$ (3)

Space group	P 2 ₁ /n
a, Å	8.842(2)
b, Å	13.830(4)
c, Å	9.910(3)
β , deg	104.45(2)
V, Å ³	1173.5(5)
Z	4
ρ_{calc}	1.38
μ , cm ⁻¹ (Mo K α)	8.3

Data collection

Radiation	Mo K α
λ , Å	0.71069
Mode	$\theta:2\theta$
2θ range, deg	3.0 - 57.5
Scan range, deg	0.8(1), 0.9(r)
Scan speed, deg/min	3.0 - 16.0
Scan/background	0.75
Exposure (hr.)	87.92
Reflections	3795

Agreement factors

R^a	0.0371
R_w^b	0.0396
S	0.00095
Maximum peak in final difference map (e ⁻ Å ⁻³)	0.51 _c

$$^a R = \Sigma (|F_o - F_c|) / \Sigma (F_o)$$

$$^b R_w = \Sigma (w^{1/2} |F_o - F_c|) / \Sigma (w^{1/2} F_o),$$

$$w = (\sigma^2(F) + g F^2)^{-1}$$

_c Largest peak is 0.5 Å from H13A. Next largest peak is 0.32 e⁻ Å⁻³.

Table II. Atomic Coordinates and Thermal Parameters for $[\text{Mo}(\text{dape})_2(\text{OCHO})_2]_n^a$

<u>Atom</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>U_{equiv}</u>
Mo(1)	0	0	0	48(1)
P(1)	2363(2)	1269(1)	1129(2)	72(1)
P(2)	926(2)	-191(1)	2431(1)	68(1)
Ox(1)	-1736(5)	1083(3)	-85(4)	81(2)
C(11)	1645(9)	2499(4)	602(7)	115(5)
Ca	-3319(9)	1372(5)	-943(8)	97(4)
Ha	-3511(78)	2005(38)	-635(56)	106 ^b
Ox(2)	-4383(6)	1055(4)	-2088(6)	167(4)
C(21)	2763(10)	671(5)	3533(6)	116(5)
C(22)	-750(10)	103(6)	2810(8)	122(5)
C(12)	4404(9)	1251(7)	1150(11)	181(9)
C(23)	1885(10)	-1309(4)	3398(6)	116(4)
C(13)	3220(15)	1317(7)	2957(7)	229(8)

^aFractional atomic coordinates ($\times 10^4$). The equivalent isotropic U ($\text{\AA}^2 \times 10^3$) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b $U_{iso}(\text{Ha}) = 1.2 \times U_{equiv}(\text{Ca})$.

Table III. Bond Lengths (Å) within [Mo(dmpc)₂(OCHO)₂]

Mo(1)-P(1)	2.467(1)	Mo(1)-P(2)	2.472(2)
	Mo(1)-Ox(1)	2.102(4)	
Ox(1)-Ca	1.247(7)	Ca-Ox(2)	1.203(9)
	Ca-Ha	0.993(61)	
P(1)-C(11)	1.793(6)	P(2)-C(21)	1.836(6)
P(1)-C(12)	1.788(11)	P(2)-C(22)	1.807(11)
P(1)-C(13)	1.811(8)	P(2)-C(23)	1.816(6)
	C(21)-C(13)	1.304(14)	

Table IV. Bond Angles (deg.) within $[\text{Mo}(\text{dmpc})_2(\text{OCHO})_2]$ ^a

P(1)-Mo(1)-P(2)	79.9(1)	P(1)-Mo(1)-P(2a)	100.1(1)
P(1)-Mo(1)-Ox(1)	84.3(1)	P(1)-Mo(1)-Ox(1a)	95.7(1)
P(2)-Mo(1)-Ox(1)	84.2(1)	P(2)-Mo(1)-Ox(1a)	95.8(1)
Mo(1)-P(1)-C(11)	117.0(2)	Mo(1)-P(2)-C(21)	109.2(3)
Mo(1)-P(1)-C(12)	123.1(3)	Mo(1)-P(2)-C(22)	117.1(2)
Mo(1)-P(1)-C(13)	109.1(4)	Mo(1)-P(2)-C(23)	122.7(3)
C(11)-P(1)-C(12)	100.4(4)	C(21)-P(2)-C(22)	102.2(4)
C(11)-P(1)-C(13)	101.7(4)	C(21)-P(2)-C(23)	101.0(3)
C(12)-P(1)-C(13)	102.8(5)	C(22)-P(2)-C(23)	101.7(4)
P(1)-C(13)-C(21)	121.8(6)	P(2)-C(21)-C(13)	119.3(5)
Mo(1)-Ox(1)-Ca	136.7(5)	Ox(1)-Ca-Ox(2)	127.3(8)
Ox(1)-Ca-Ha	109.4(26)	Ha-Ca-Ox(2)	122.1(27)

^aAtoms with numbers having 'a' subscripts are symmetry generated by the center of inversion.

Table V. Infra Absorptions (cm^{-1}) of the Functional Groups in Products Derived from the Reaction of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with CO_2 and of their ^{13}C and D labelled Analogs in Nujol, Benzene, and Pentane^a

Complex	Nujol				
	$\nu_{\text{O}_2\text{C-H(D)}}$	$\nu_{\text{Mo-H}}$	ν_{CO_2}	ν_{CO_3}	$\nu_{\text{OCH(D)=O}}$
$[\text{Mo}(\text{dmpe})_2\text{H}_4] \text{ (1)}$	-	1743 w sh, 1725 w sh, 1701 m, 1679 ms	-	-	-
$[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2] \text{ (2)}$	-	1800 w br	-	1656 w, 1601 s	-
$[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{D}_2]$	-	-	-	1656 w, 1601 s	-
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_3)\text{H}_2]$	-	1800 w br	-	- ^b , 1561 s	-
$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2] \text{ (3)}$	2704 w	-	-	-	1614 s
$[\text{Mo}(\text{dmpe})_2(\text{OCDO})_2]$	- ^c	-	-	-	1604 s
$[\text{Mo}(\text{dmpe})_2(\text{O}^{13}\text{CHO})_2]$	2696 w	-	-	-	1576 s
$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}] \text{ (4)}$	2682 w	1891 w br	1787 ms, 1744 s	-	1614 s
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_2)(\text{O}^{13}\text{CHO})\text{H}]^{\text{d}}$	not obs.	not obs.	1747	1704	1576

$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3] \quad (5)$	2689 w	1843 w br	1628 s	-	1612 s
$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCDO})\text{D}_3] \quad -^c$	-	-	1624 s ^e	-	1602 s
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_2)(\text{O}^{13}\text{CHO})\text{H}_3]$	2682 w	1843 w br	1588 s	-	1574 s
$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2] \quad (6)$	not obs.	1757 w, 1740 w	-	-	1653 s
$[\text{Mo}(\text{dmpe})_2(\text{OCDO})_2\text{D}_2]$	no solid samples				
$[\text{Mo}(\text{dmpe})_2(\text{O}^{13}\text{CHO})_2\text{H}_2]$	no solid samples				

Benzene

$[\text{Mo}(\text{dmpe})_2\text{H}_2] \quad (1)$	-	-f	-	-	-
$[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{H}_2] \quad (2)$	-	-f	-	1655 w, 1636 s	-
$[\text{Mo}(\text{dmpe})_2(\text{CO}_3)\text{D}_2]$	-	-	-	1655 w, 1636 s	-
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_3)\text{H}_2]$	-	-f	-	not obs., 1590 s	-
$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2] \quad (3)$	2702 w	-	-	-	1618 s
$[\text{Mo}(\text{dmpe})_2(\text{OCDO})_2] \quad -^c$	-	-	-	-	1611
$[\text{Mo}(\text{dmpe})_2(\text{O}^{13}\text{CHO})_2]$	not obs.	-	-	-	1580

$[\text{Mo}(\text{dmpe})_2(\text{CO})_2(\text{OCHO})\text{H}]$ (4)	2702	^f -	1794 ^g , 1745 ^g	-	1618
$[\text{Mo}(\text{dmpe})_2(\text{CO})_2(\text{OCHO})\text{H}_3]$ (5)	not obs.	^f -	1667 s	-	1629
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO})_2(\text{O}^{13}\text{CHO})\text{H}_3]$	not obs.	^f -	1625 s	-	1587
$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ (6)	not obs.	^f -	-	-	1618
$[\text{Mo}(\text{dmpe})_2(\text{OCDO})_2\text{D}_2]$	^c -	-	-	-	1611
$[\text{Mo}(\text{dmpe})_2(\text{O}^{13}\text{CHO})_2\text{H}_2]$	not obs.	^f -	-	-	1580

Pentane

$[\text{Mo}(\text{dmpe})_2\text{H}_4]$ (1)	-	1702 sh, 1685 s	-	-	-
$[\text{Mo}(\text{dmpe})_2(\text{CO})\text{H}]$ (2)	insoluble in pentane				
$[\text{Mo}(\text{dmpe})_2(\text{CO})\text{D}_2]$	insoluble in pentane				
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO})_2\text{H}_2]$	insoluble in pentane				
$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$ (3)	2702 w	-	-	-	1624 s
$[\text{Mo}(\text{dmpe})_2(\text{OCDO})_2]$	^c -	-	-	-	1614
$[\text{Mo}(\text{dmpe})_2(\text{O}^{13}\text{CHO})_2]$	not obs.	-	-	-	1586

$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}]$ (ν)	2702	not obs.	1812, 1768	-	1624
$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{H}_3]$ (ν)	not obs.	not obs.	1685 s	-	1624
$[\text{Mo}(\text{dmpe})_2(\text{CO}_2)(\text{OCHO})\text{D}_3]$	-	-	1685 s	-	1614
$[\text{Mo}(\text{dmpe})_2(^{13}\text{CO}_2)(\text{O}^{13}\text{CHO})\text{H}_3]$	not obs.	not obs.	1643 s	-	1586
$[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2\text{H}_2]$ (ν)	not obs.	not obs.	-	-	1624
$[\text{Mo}(\text{dmpe})_2(\text{OCDO})_2\text{D}_2]$	-	-	-	-	1614
$[\text{Mo}(\text{dmpe})_2(\text{O}^{13}\text{CHO})_2\text{H}_2]$	not obs.	not obs.	-	-	1586

a Many of the absorptions in pentane or benzene were determined from mixtures of materials (particularly in the case of labelled samples). This sometimes resulted in the overlap of absorptions from different species, and intensity estimates have been omitted in such cases. All assignments are consistent with the labelling studies, as discussed in the text. The notation "not obs." indicates that a weak absorption would have been anticipated from this functional group in a complex, but that experimental limitations precluded observation of the absorption. In every case in which a strong absorption was anticipated an appropriate band was observed with appropriate isotopic shifts.

b The $^{13}\text{C}=\text{O}$ band corresponding to the weak 1656 cm^{-1} absorption in unlabelled $\underline{2}$ was obscured by the strong 1601 cm^{-1} absorption of some unlabelled $\underline{2}$ in the sample.

c Formate C-D stretches were in general obscured by absorptions assigned to partially deuterated dmpe ligands.

d This sample was contaminated by some $\underline{3}$.

e See Results and Discussion for the origin of this shift.

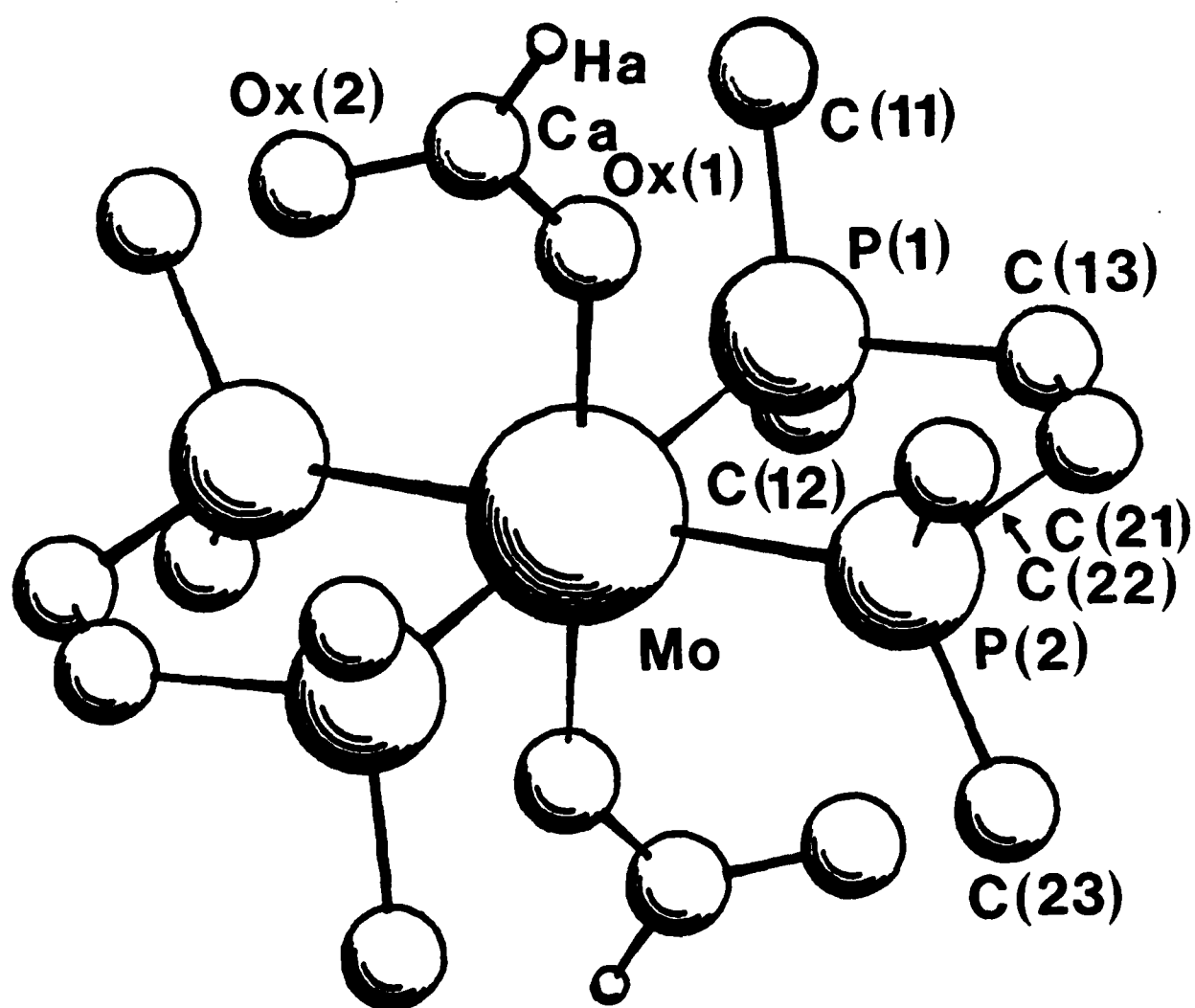
f Weak absorptions in the 1800 cm^{-1} region would have been obscured in this solvent.

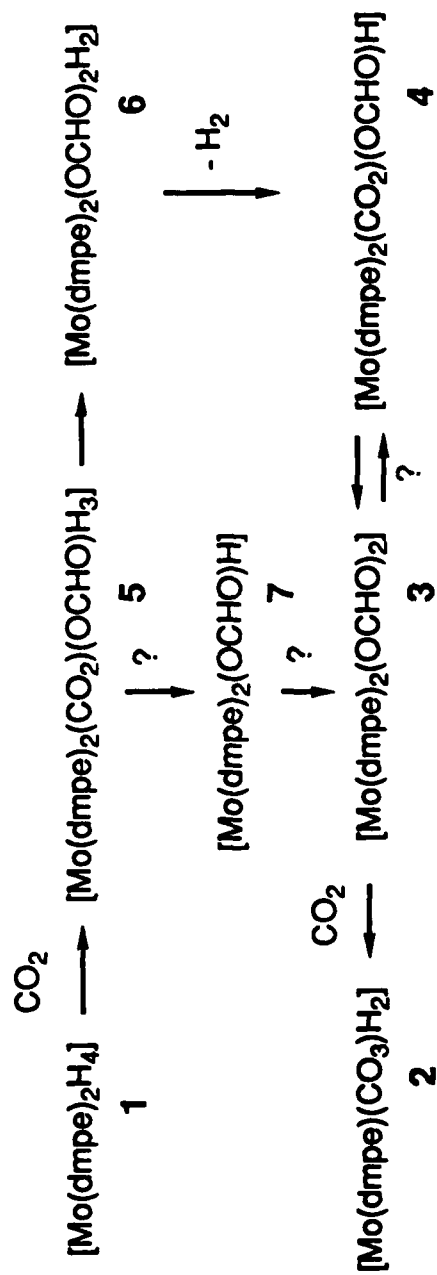
g Recorded in d_6 -benzene, which has a window in this region.

Figure 1. SNOOPI drawing of $[\text{Mo}(\text{dmpe})_2(\text{OCHO})_2]$, indicating atomic nomenclature.

Atoms have been drawn at 50% of their covalent radii, and dmpe hydrogen atoms have been omitted for clarity.

Scheme I. Most probable relationships between complexes derived from the reaction of $[\text{Mo}(\text{dmpe})_2\text{H}_4]$ with CO_2 .





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